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# S-functionalized MXenes as Electrode Materials for Li-Ion Batteries

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## Abstract

MXenes are promising electrode materials for Li-ion batteries because of their high Li capacities and cycling rates. We use density functional theory to investigate the structural and energy storage properties of Li decorated  $\text{Zr}_2\text{C}$  and  $\text{Zr}_2\text{CX}_2$  ( $\text{X} = \text{F}, \text{O}$  and  $\text{S}$ ). We find for  $\text{Zr}_2\text{C}$  and  $\text{Zr}_2\text{CS}_2$  high Li specific capacities and low diffusion barriers. To overcome the critical drawbacks of the OH, F, and O groups introduced during the synthesis we propose substitution by S groups and demonstrate that an exchange reaction is indeed possible.  $\text{Zr}_2\text{CS}_2$  shows a similar Li specific capacity as  $\text{Zr}_2\text{CO}_2$  but a substantially reduced diffusion barrier.

**Keywords:**  $\text{Zr}_2\text{C}$ , MXene, Functionalization, Li-ion battery, Capacity, Diffusion

# 1 Introduction

Numerous two-dimensional materials, including boron nitride,<sup>1</sup> transition metal chalcogenides,<sup>2</sup> and silicene,<sup>3</sup> are products of the graphene era.<sup>4–6</sup> MXenes<sup>7–11</sup> form a rather new class of two-dimensional carbides and/or carbonitrides<sup>12</sup> with numerous potential applications in sensors, electronic devices, optoelectronic devices, supercapacitors, or as catalyst materials.<sup>13–18</sup> MXenes are commonly synthesized by selective etching of the A metal from the three-dimensional  $M_{n+1}AX_n$  phases (where  $n = 1, 2, 3, 4$ , M is an early transition metal, A is a group 13–16 element, and X is C and/or N).<sup>19,20</sup> The  $M_{n+1}AX_n$  phases have hexagonal structures (space group  $P63/mmc$ ), which are composed of  $n$  “ceramic” MX layer(s) alternating with the “metallic” A layer. The combination of ceramic (high decomposition or melting temperature, high elastic stiffness, and good machinability) and metallic (high thermal shock resistance and good thermal and electrical conductivities) characteristics leads to widely applicable materials.

The main drive for the investigation of MXenes as electrode materials for Li-ion batteries is the high Li storage capacity, which is comparable to the commercial graphite electrodes.<sup>21</sup> Small Li diffusion barriers additionally result in high cycling rates.<sup>21,22</sup> Most metallic MXenes provide a high electrical conductivity.<sup>23</sup>  $Ti_2C$  has been predicted to be stable during the Li adsorption process<sup>24</sup> and dimethylsulfoxide intercalation has been demonstrated to improve the Li capacity of  $Ti_3C_2$ .<sup>25</sup> Concerning materials simulations, Xie and Kent<sup>26</sup> have shown that the Perdew-Burke-Ernzerhof (PBE) and Heyd-Scuseria-Ernzerhof (HSE06) functionals result in similar structural and electronic properties for  $Ti_{n+1}C_n$  ( $n = 1$  to 9), even though the HSE06 functional often is deemed to be more accurate.

Although the MXene family grows continuously and consists of various types of compounds ( $M = Sc, Ti, V, Cr, Zr, Nb, Hf$ , and  $Ta$ ),<sup>27,28</sup> only the titanium carbides have been investigated systematically.<sup>21,24–26,29</sup> Reports on the performance of other MXenes are scarce. In the case of  $V_2C$  a Li capacity of 941 mAh/g has been predicted when considering multilayer Li adsorption, which is considerably higher than the experimental value of 260 mAh/g.<sup>30</sup> The successful preparation of  $Zr_{n+1}AX_n$  phases<sup>31,32</sup> paves the way to Zr-based MXenes, as the synthesis of MXenes from the respective bulk materials is well established. Indeed, Zr-based MXenes are likely to be realized more easily than their Ti and Nb counterparts because of larger differences in the bonding strength within the  $ab$ -plane and along the  $c$ -axis.<sup>33</sup> Inevitably, OH, F, and O groups cap the MXene during

preparation due to the presence of HF and H<sub>2</sub>O.<sup>34</sup> These hard nucleophiles may bind to Li to form byproducts, which obstruct Li diffusion.<sup>35</sup> In the present study we investigate the applicability of Zr<sub>2</sub>C, a material that so far has escaped attention, for Li-ion batteries, focusing on new capping elements, including S, Se, and Te.

## 2 Computational method

The calculations are performed in the framework of density functional theory using the projector augmented wave method as implemented in the Vienna Ab-initio Simulation Package.<sup>36</sup> The generalized gradient approximation (PBE flavor) is selected for the exchange-correlation potential.<sup>37</sup> Brillouin zone integrations are performed on  $6 \times 6 \times 1$  and  $12 \times 12 \times 1$  k-meshes, respectively, for the geometry optimization and electronic structure calculations. A cut-off energy of 500 eV for the plane wave basis is found to yield converged results. The energy criterion for the iterative solution of the Kohn-Sham equations is set to  $10^{-6}$  eV. All structures are relaxed until the residual forces on the atoms have declined to less than 0.01 eV/Å. A  $2 \times 2 \times 1$  supercell of monolayer Zr<sub>2</sub>C is used to model Li decoration, where a vacuum layer of 15 Å thickness is found to be sufficient to avoid unphysical interaction between images due to the periodic boundary conditions. We have tested for the Li diffusion barriers that the results for a  $3 \times 3 \times 1$  supercell deviate by less than 5%. The nudged elastic band method<sup>38</sup> with 7 to 9 images between the initial and final configurations is applied to calculate the energy barriers of Li diffusion and thus to determine the minimum energy paths.

Reaction enthalpies  $\Delta_r H$  are derived from the computed bulk/molecular total energies of the reactants and products: -41.203 eV for Zr<sub>2</sub>CF<sub>2</sub>, -47.358 eV for Zr<sub>2</sub>CO<sub>2</sub>, -40.087 eV for Zr<sub>2</sub>CS<sub>2</sub>, -32.656 eV for S<sub>8</sub>, -3.557 eV for F<sub>2</sub>, -9.858 eV for O<sub>2</sub>, -22.953 eV for CO<sub>2</sub>, -16.220 eV for CS<sub>2</sub>, -19.828 eV for COS, -11.202 eV for H<sub>2</sub>S, and -14.219 eV for H<sub>2</sub>O. The cohesive energy of Zr<sub>2</sub>CS<sub>2</sub> is calculated to be 4.95 eV/atom, reflecting chemical stability. Gibbs energies  $\Delta_r G$  are calculated using the gas phase entropies at the respective temperatures, which are available from the NIST database, except for the MXenes.<sup>39</sup> We assume that i) an entropic contribution of the MXenes to the overall thermochemistry of the conversions can be neglected due to very similar compositions and structures, ii) all reactants are in the gas phase with the exception of the solid MXenes, which is reasonable as similar conversions typically require elevated temperatures and gaseous reactants can well access the MXene surface, and iii)  $\Delta_r H$  is constant within a synthetically reasonable temperature range.

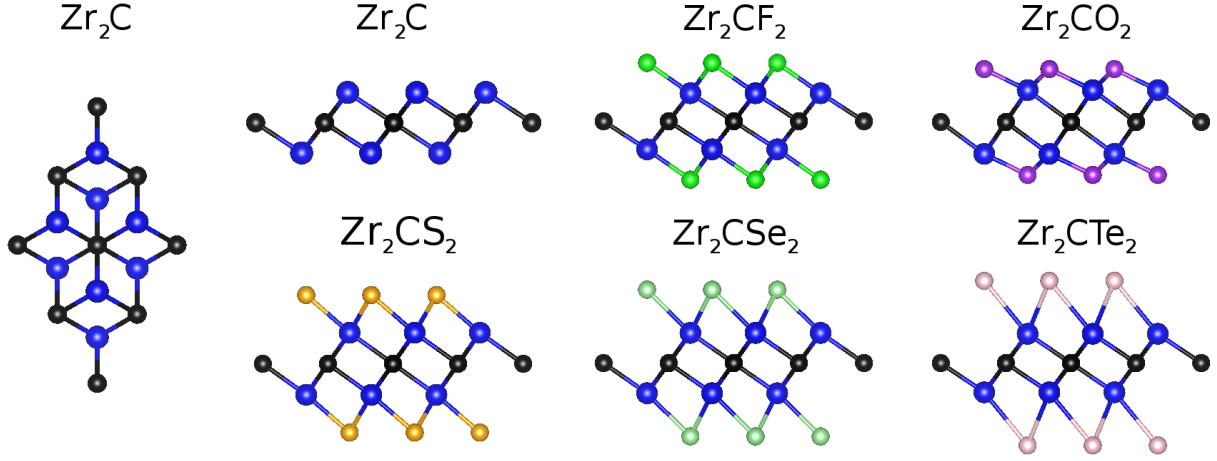


Figure 1: Structures of  $\text{Zr}_2\text{C}$  and  $\text{Zr}_2\text{CX}_2$  ( $\text{X} = \text{F}, \text{O}, \text{S}, \text{Se}, \text{and Te}$ ) (left: top view, others: side view). The Zr, C, F, O, S, Se, and Te atoms are shown in blue, black, green, purple, brown, cyan, and pink color.

Applying available gas phase enthalpy corrections,<sup>39</sup>  $\Delta_r H$  changes by less than 1.4 kcal/mol between 300 and 1000 K.

### 3 Results and discussion

Figure 1 shows the structures of  $\text{Zr}_2\text{C}$  and  $\text{Zr}_2\text{CX}_2$  ( $\text{X} = \text{F}, \text{O}, \text{S}, \text{Se}, \text{and Te}$ ). Non-magnetic, ferromagnetic, and antiferromagnetic calculations are performed in the case of the bare MXene. Antiferromagnetism with parallel spins within each Zr layer but opposite spins in the top and bottom Zr layers is found to constitute the ground state (10 meV per atom lower energy than ferromagnetism), which contradicts previous calculations<sup>28</sup> that have used a weaker energy criterion for the self-consistency ( $10^{-4}$  eV). The in-plane lattice constant of  $\text{Zr}_2\text{C}$  is calculated to be 3.317 Å, which is in agreement with a previous theoretical result (3.269 Å).<sup>40</sup> Added capping elements can be located on top of the C, Zr(1) (top Zr layer), and Zr(2) (bottom Zr layer) atoms, on both sides of the MXene. All groups favor to be located on top of the C atoms (coordinated equidistantly to three neighbouring Zr atoms), which results in a non-magnetic state. The Zr(1)-X bond lengths are calculated to be 2.12, 2.53, 2.69, and 3.01 Å for O, S, Se, and Te functionalization, respectively, reflecting the different ionic radii. The Zr-F bond (2.33 Å) is longer than the Zr-O bond due to the different oxidation states of the anionic capping elements. The higher negative charge of the O group results in a stronger Coulombic interaction to the positively charged Zr atoms.

Li can be located on top of the C, Zr(1), and Zr(2)/X atoms. Energetical favorable is Zr(2) for

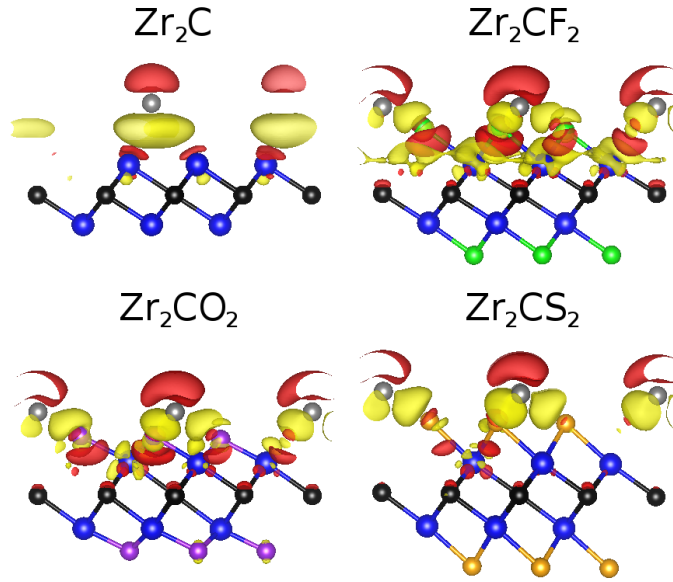


Figure 2: Charge redistribution due to the interaction with Li. Yellow/red color represents charge accumulation/depletion, where the isosurfaces refer to an isovalue of  $2 \times 10^{-3}$  electrons/bohr<sup>3</sup>. The Zr, C, Li, F, O, and S atoms are shown in blue, black, grey, green, purple, and brown color.

the bare MXene, C for F/O/S passivation, and Zr(1) for Se/Te passivation. The Li-X bond lengths are calculated to be 1.86, 2.04, 2.29, 2.41, and 2.62 Å for F, O, S, Se, and Te, respectively, due to increasing atomic radii. The stability of a phase is given by its formation energy with respect to a reference material,

$$\Delta H = E - E_{\text{MXene}} - E_{\text{reference}}, \quad (1)$$

where  $E$  is the total energy of the full system,  $E_{\text{MXene}}$  the total energy of the MXene without Li, and  $E_{\text{reference}}$  the total energy of the reference material (bulk Li and Li<sub>2</sub>X). The capping atoms may form byproducts with Li. For the F group and one Li atom with respect to LiF and the O, S, Se, and Te groups and two Li atoms with respect to Li<sub>2</sub>X (X = O, S, Se, and Te) we obtain formation energies of -0.25, -2.62, -1.06, 0.55, and 2.88 eV, respectively. Negative values indicate an exothermic process. The instability of the Se and Te terminations when Li atoms are added is a consequence of the larger Zr-Se and Zr-Te bond lengths. Since capping with Se and Te atoms is unstable in Li environment, these cases will not be considered in the following. For decoration with a single Li atom with respect to bulk Li we obtain values of -0.34, -1.05, -1.70 and -2.07 eV for Zr<sub>2</sub>C and Zr<sub>2</sub>CX<sub>2</sub> (X = F, O and S), respectively. The positive value of 0.88 eV in the case of Zr<sub>2</sub>C(OH)<sub>2</sub> points to the formation of Li clusters.<sup>35</sup>

Further insight into the stability can be obtained from the charge density differences shown in

Table 1: Partial atomic charges (in electrons) calculated by the Bader approach for  $\text{Zr}_2\text{C}$  and  $\text{Zr}_2\text{CX}_2$  ( $\text{X} = \text{F}, \text{O}, \text{and S}$ ).

	bare	F	O	S
Li	+0.81	+0.88	+0.87	+0.86
X		-0.85	-1.35	-1.08
Zr(1)	+0.82	+1.74	+2.15	+1.84
C	-2.19	-2.14	-1.98	-1.94

Figure 2, defined as

$$\Delta\rho = \rho - \rho_{\text{MXene}} - \rho_{\text{Li}}, \quad (2)$$

where  $\rho$ ,  $\rho_{\text{MXene}}$ , and  $\rho_{\text{Li}}$  are the charge densities of the full system, the MXene without Li, and an isolated Li atom, respectively. In the case of the bare MXene the charge redistribution towards Li is significantly different from the cases of the passivated MXenes, reflecting differences in the interaction. For the passivated MXenes, the charge redistribution becomes smaller from F to S because of the decreasing electronegativity. Mostly the Zr(1) and X ( $\text{X} = \text{F}, \text{O}, \text{and S}$ ) atoms are affected. Table 1 lists partial atomic charges calculated by the Bader approach. A higher charge redistribution indicates a stronger polarization of the electronic shells of the X atoms and this in turn an enhanced covalency for the X-Li interaction, which explains the less negative formation energy for Li decoration described above. The densities of states shown in Figure 3 demonstrate increasing hybridization between the X  $p$  and Li  $s$  states (enhanced covalent interaction) from  $\text{X} = \text{F}$  to S.

The charging rate depends on the diffusion properties of Li. Three diffusion paths are considered, where the ground state position of Li and its nearest neighbor positions are the initial and final states. Path I/II passes the top of the C/Zr(1) and Zr(1)/X atoms, respectively, for the bare and F/O/S passivated MXenes, whereas path III directly connects the initial and final states. Path I, see Figure 4, exhibits a lower diffusion barrier than path II for all cases due to the strong interaction at the transition states. Path III always converges to path I. The diffusion barrier for Li along path I is compared in Figure 5.  $\text{Zr}_2\text{C}$  shows the lowest value of 34 meV due to flat a surface charge distribution with the transition state located on top of the Zr(2)-C bond. There is a local minimum (17 meV) on top of the C atom. In the other cases the diffusion barriers are much higher, where the transition state is located on top of the Zr(1) atom for  $\text{Zr}_2\text{CO}_2$  and on top of the Zr(1)-C bond for  $\text{Zr}_2\text{CF}_2$  and  $\text{Zr}_2\text{CS}_2$ . Presence of many OH groups can be expected because of the synthesis in water.<sup>41</sup> Although this group can be converted into an O group by high temperature annealing to improve the Li stability,<sup>35</sup> the semiconducting character<sup>23</sup> and high diffusion barrier still limit the

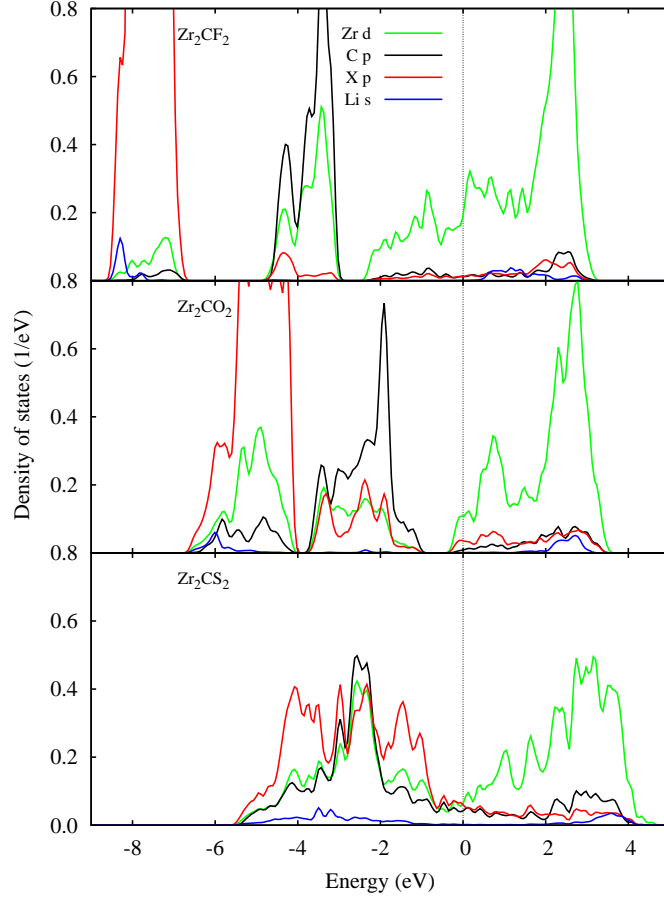
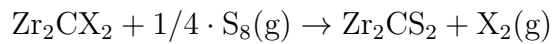


Figure 3: Densities of states for  $\text{Zr}_2\text{CX}_2$  ( $\text{X} = \text{F}$ ,  $\text{O}$ , and  $\text{S}$ ) after Li decoration. The Fermi level is set to zero.

applicability of the material. In contrast,  $\text{Zr}_2\text{CS}_2$  is found to be metallic, which is crucial for battery applications.

However, our calculations indicate that exchanging the OH, F, and O groups on the  $\text{Zr}_2\text{C}$  surface sheet for S should overcome these drawbacks. We expect that such an exchange should indeed be experimentally feasible. Qualitatively, the conductive  $\text{Zr}_2\text{C}$  has a high electron density and correspondingly the Zr atoms should be considered rather soft Lewis metal centers unlike the  $\text{Zr(IV)}$  ions in typical Zr salts, resulting in a preference for the soft S over the hard F and O anions. To evaluate which reagent might allow the synthesis of  $\text{Zr}_2\text{CS}_2$ , we estimate the thermochemistry for conversions of the respective MXenes from a combination of computational and experimental data.<sup>39</sup>

Concerning the interconversions of the MXenes with elemental S, we find strongly endothermic reactions



132/128 kcal/mol for  $\text{X} = \text{F}/\text{O}$ . A temperature above 600 K would be required to achieve a reasonable



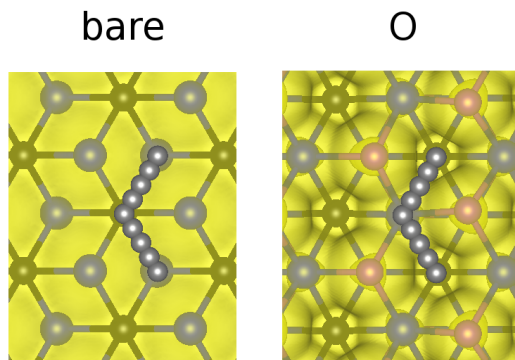


Figure 4: Diffusion paths for Li atoms. The Zr, C, Li, and F/O/S atoms are shown in blue, black, grey, and purple color. The surface charge distribution is shown in yellow for the O case. For the F and S cases the distribution is virtually the same.

vapor pressure of  $S_8$  (and smaller  $S_n$  molecules) in the gas phase.<sup>42</sup> For  $X = F/O$  we obtain  $\Delta_r G$  values of 125/121 kcal/mol at 298 K, 119/115 kcal/mol at 600 K, and 115/112 kcal/mol at 800 K. Correspondingly, a reagent with a strongly exergonic S/O-exchange is necessary to drive the reaction.  $H_2S$  as S transfer reagent cannot provide the free energy required



( $\Delta_r H^0 = -99.9$  kcal/mol,  $\Delta_r G^0 = -91.4$  kcal/mol) so that a treatment of the MXenes with  $H_2S$  is not sufficient. A more exothermic S/O-exchange reagent should react with water under release of  $H_2S$ .  $CS_2$  is known to hydrolyze<sup>43,44</sup> under formation of  $CO_2$  and  $H_2S$ . Its formal conversion to COS



( $\Delta_r H^0 = -127.2$  kcal/mol,  $\Delta_r G^0 = -119.8$  kcal/mol) can provide the necessary free energy. The interconversion of  $Zr_2CO_2$  with  $CS_2$  to  $Zr_2CS_2$  under the release of COS should therefore be nearly thermoneutral and feasible, for example by applying an excess of S. The calculated  $\Delta_r G$  for this reaction is 1.7 kcal/mol at 298 K, 2.6 kcal/mol at 600 K, and 3.2 kcal/mol at 800 K. The exchange of both S atoms in  $CS_2$  for O is slightly less exothermic



( $\Delta_r H^0 = -116.0$  kcal/mol,  $\Delta_r G^0 = -107.4$  kcal/mol) so that the  $Zr_2CO_2/Zr_2CS_2$  interconversion

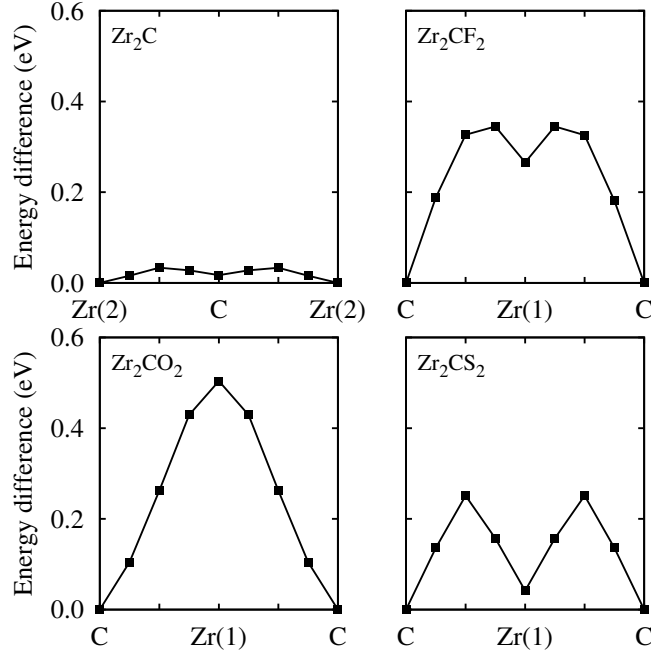


Figure 5: Diffusion barriers for Li atoms on  $Zr_2C$  and  $Zr_2CX_2$  ( $X = F, O$ , and  $S$ ).

under the release of  $CO_2$  is moderately endergonic (14.1 kcal/mol at 298 K, 16.7 kcal/mol at 600 K, and 18.5 kcal/mol at 800 K). Literature provides evidence that the above reactions are kinetically feasible.  $CS_2$  has a rich chemistry with transition metals and readily inserts into MO bonds.<sup>45</sup> Correspondingly,  $CS_2$  has been used as a less toxic replacement of  $H_2S$  in the preparation of metal-sulfides from oxides, for example in the synthesis of  $ZrS_2$ ,<sup>46</sup> the full or partial S/O-exchange in spinel  $Li_4Ti_5O_{12}$ , and the preparation of other transition metal sulfides.<sup>47–49</sup>

A high Li specific capacity (ability to absorb Li atoms) is crucial for usage of MXenes as anode material. We consider adsorption up to a monolayer of Li on both sides of the MXene as our aim is to demonstrate the effects of the functional group. The real capacity will be higher, because the Li atoms can arrange in multilayers.<sup>30</sup> The open circuit voltage as a function of the Li coverage is addressed in Figure 6. For  $Zr_2CLi_x$  the voltage is approximately 0.4 V,  $Zr_2CO_2Li_x$  delivers a maximal voltage of 2.5 V when 3 Li atoms are located on each side of the MXene ( $x = 1.5$ ), and the voltage decreases continuously for  $Zr_2CS_2Li_x$ .  $Zr_2CS_2$  can absorb up to 10 Li atoms per  $2 \times 2 \times 1$  supercell without forming clusters, see Figure 7, where 8 are located on top or bottom of C atoms and 2 on top of Zr(1) atom, corresponding to 2.5 Li atoms per unit cell.  $Zr_2C$  and  $Zr_2CO_2$  can accommodate 9 Li atoms (2.25 Li atoms per unit cell), whereas  $Zr_2CF_2$  can accommodate only 2 Li atoms without

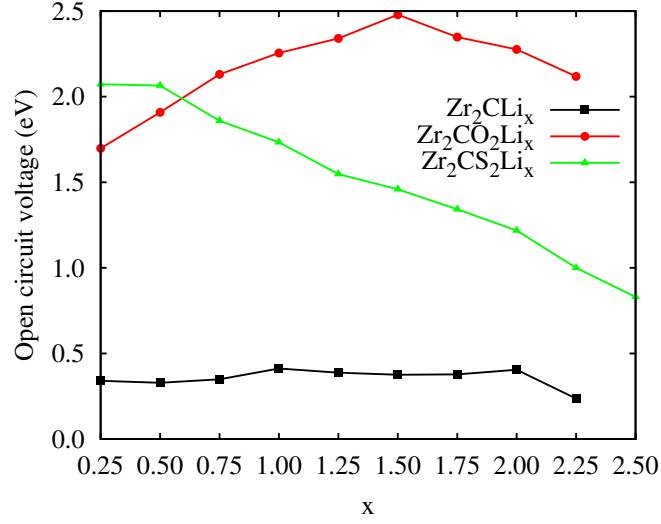


Figure 6: Open circuit voltage for  $\text{Zr}_2\text{C}$  and  $\text{Zr}_2\text{CX}_2$  ( $\text{X} = \text{O}$  and  $\text{S}$ ) as a function of the Li coverage.

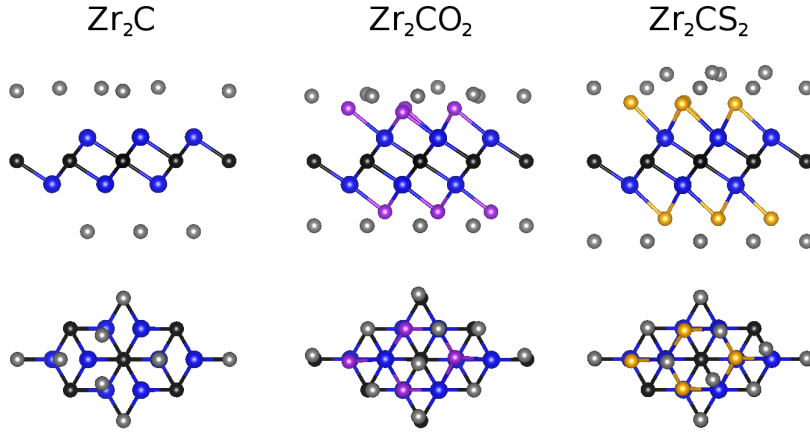


Figure 7: Side and top views of fully lithiated  $\text{Zr}_2\text{C}$ ,  $\text{Zr}_2\text{CO}_2$ , and  $\text{Zr}_2\text{CS}_2$ . The Zr, C, O, S, and Li atoms are shown in blue, black, purple, brown, and grey color.

forming  $\text{LiF}$ , as reported previously for  $\text{Ti}_3\text{C}_2$  and  $\text{V}_2\text{C}$ .<sup>22,30</sup> The Li specific capacity is given by

$$C = \frac{x \cdot F}{M}, \quad (3)$$

where  $M$  is the atomic mass of  $\text{Zr}_2\text{CX}_2$  and  $F$  is the Faraday constant. We obtain 310 mAh/g for  $\text{Zr}_2\text{C}$ , 266 mAh/g for  $\text{Zr}_2\text{CO}_2$  and 259 mAh/g for  $\text{Zr}_2\text{CS}_2$ . These values are comparable to the high Li specific capacity of  $\text{Ti}_3\text{C}_2$  (320 mAh/g).<sup>22</sup> A much lower value of 58 mAh/g is obtained for  $\text{Zr}_2\text{CF}_2$ . Importantly, the S group provides a similar performance as the O group.

## 4 Conclusions

Our comparative study of Li decoration of  $\text{Zr}_2\text{C}$  and  $\text{Zr}_2\text{CX}_2$  ( $\text{X} = \text{OH}, \text{F}, \text{O}, \text{S}, \text{Se}, \text{and Te}$ ), for evaluating possibilities and limitations of application in Li-ion batteries shows that the charge redistribution at the interface between Li and the functional group of the MXene decreases from F to S, following the electronegativity trend. Li specific capacities of 310 and 259 mAh/g are obtained for  $\text{Zr}_2\text{C}$  and  $\text{Zr}_2\text{CS}_2$ , respectively, which are very promising values.  $\text{Zr}_2\text{CS}_2$  shows a substantially reduced diffusion barrier but similar Li specific capacity as  $\text{Zr}_2\text{CO}_2$ . Nowadays OH, F, and O groups attached to the surface are inevitable during the preparation of MXenes. Their replacement with S groups is predicted to result in high electric conductivities and cycling rates (minor structural distortions, low diffusion barriers) for Li-ion batteries using Zr-based MXenes. In addition, byproducts affecting the lifetime are avoided. Importantly, the replacement is compatible with present synthesis techniques, since it can be applied to the as-prepared MXenes. While OH groups can be converted into O groups by high temperature annealing, O and F groups can be replaced by S groups via moderately endergonic and kinetically feasible reactions with  $\text{CS}_2$  in solution. Zr-based MXenes therefore are predicted to form a class of highly promising electrode materials for Li-ion batteries.

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